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Subject: Primary Processes R & D  
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### BASIC RESOURCES RESEARCH

#### AD-117 - Impurity Leaching Process

An experimental program designed to test the effect of alumina calcination temperature, hydrochloric acid, hydrofluoric acid and added organic alcohol (methyl-iso-butylcarbinol, glycerine or sucrose) on the leachability of phosphorus from alumina was carried out. No significant reduction in  $P_2O_5$  level was achieved. A new campaign of experiments based on the known mechanism of phosphate binding to the surfaces of kaolin particles has been begun. The problems associated with colorimetric determination of low levels of  $P_2O_5$  are being resolved by the analytical laboratory.

#### AD-105 - Alumina Process

A leaching study examining the response of alumina and impurity extraction efficiencies vs time, temperature, ammonia concentration and leaching method has been completed. The chemical analysis is complete and the evaluation of the results is underway.

A decomposition study was performed on ammonoalunite precipitated from synthetic solutions. From the weight loss and chemical analyses, it appears that ammonoalunite decomposes according to the previously reported equations. Ammonia can be recovered at temperatures from 450-500°C. At least 40 percent of the sulfur is evolved as  $SO_3$ .

X-ray analysis of ammonoalunite calcined at 1000°C and 1150°C show that the 1000°C sample is 90%+ gamma alumina and the 1150°C sample is essentially 100% alpha alumina.

#### AD-118 - F-Activated Leach

The mass balance on fluoride ion in the leach of raw clay by  $HCl/H_2SiF_6$  solution shows about 50% loss of fluoride with the silica residues. This is similar to results obtained by others in a sulfuric acid process.

#### AD-120 - $AlCl_3$ Process

The results from  $2^3$  factorial design experiments involving the partial calcination of green petroleum coke to determine the effect of temperature, calcination time, and particle size on the residual hydrogen and surface area of coke indicate that; (1) temperature has the largest effect on reducing the

residual hydrogen, (2) particle size has no significant effect on hydrogen content, and (3) there is interaction between temperature and calcination time. From this set of experiments, the average residual hydrogen obtained was 0.16%  $H_2$  for calcining at 850°C for 30 minutes for particle size -100 mesh to +30 mesh. Surface area was found to be independent of factors investigated and it was 2 m<sup>2</sup>/gm. A 0.5%  $H_2$  hydrogen is acceptable in the process and does not adversely affect chlorine loss. However, the possible effect on PCB's has not been determined.

Decomposition tests of ACH and aluminum oxide trihydrate were examined as a function of temperature (400-800°C) for a two hour period. Preliminary results of residual hydrogen in the ACH indicated that the hydrogen is at least twice as high at 550°C as reported by CSIRO patent and used in the base-case economics for making anhydrous  $AlCl_3$  from PC/ACH. As a result, a campaign of 16 statistically designed experiments to determine the effect of temperature, time, particle size, heating rate and carrier gas has been undertaken. Initial samples have been sent for residual hydrogen analysis.

Chlorination rate experiments using partially calcined ACH have continued and are being compared to chlorination of MGA with fully calcined coke. The chlorination of MGA with fully calcined coke has been conducted over the temperature range of 550-800°C and extrapolated to 950°C, which is assumed to be equivalent to the Alcoa base case. An equal chlorination rate can be obtained using PC/ACH and fully calcined coke at a temperature of 730°C. The lower reaction temperature of 730°C would result in an advantage of carbon savings and a probable lower capital reactor cost as well as substantially greater reactor life.

The comparative reaction rate of PC/ACH and PC green coke at 550°C is 1.5 to 5 times the rate of the base Alcoa case depending on the analysis of  $AlCl_3$  product or materials loss in the bed. Our base-case economics used a ratio of two times the Alcoa rate which seems appropriate. Additional rate studies at temperature up to 750°C will also be run using PC/ACH and PC green coke.

A more sophisticated two-inch diameter fluid-bed reactor has been designed and will be constructed in the coming month. It should afford better comparative rate and materials balance data. When the gas chromatograph becomes operative, mass transfer coefficients can be obtained which are much more meaningful than comparative rate data.

## REDUCTION RESEARCH

### AD-108 Process

The composite powder anode has received primary attention this month in the AD-108 investigation. The only diaphragm material available has been porous graphite. Powdered compositions have been investigated consisting of separate powders of 83%  $Al_2O_3$ , 17% carbon and a powder in which the carbon is coated onto the  $Al_2O_3$ . These powders have been run in mixed chloride-fluoride melts and all-fluoride melts utilizing a variety of porous graphite anode shapes.

The conclusion of a number of experimental runs is that chlorine is evolved in the mixed chloride-fluoride melts and fluorine in the all-fluoride melt. This infers that the composite powder has such poor contact to the graphite diaphragm that the halogen is discharged in preference to the normal Hall reaction. The fact that a prebaked anode performed satisfactorily, confirms that anodic contact to the composite and wettability are the key factors to the commercial success of a powdered composite anode. The use of a non-conducting diaphragm and/or an inert anode contact could potentially solve the contact problem of powder anodes. Wettability can be achieved with melt composition once good anodic contact is achieved. Efforts are underway to obtain diaphragms of BN and AlN.

An aluminum reference electrode has been designed and tested. A standard prebaked composite anode was electrolyzed in an all fluoride melt at 738°C with an ACD of 4.13 cm. Current-voltage sweeps were made utilizing the reference electrode with respect to both the anode and cathode. At a current density of a typical modern large Hall cell (.75 amps/cm<sup>2</sup>) the overall cell voltage was 3.9V. A technique has been worked out with the Instrument Group that will allow the reference electrode to be used with an oscilloscope and separate the resistance values from electrode overvoltage. This will be coupled with a mathematical model we have developed to separate all voltage components of resistance and electrochemistry.

The experimental set-up has been completed for modeling self-baking composite anodes with various hard pitches. One test has been run and the retaining end plug failed. This problem has been corrected and additional tests are scheduled.

#### AD-116 - Potlining Resource Recovery

The AD-116 process flowsheet for potlining resource recovery was modified to include a soda ash recovery section for sodium removal from the system. An equipment list, heat and material balance was given to the process evaluation group for their capital cost estimates. In addition, an equipment flowsheet and stream flowrates for the Mini-L process were received from Alcan. The capital cost estimate for this process is nearly completed.

Laboratory work for the AD-116 process included caustic leaching of ashed potlining. A 2% sodium hydroxide solution used as the solvent increased the extraction of fluorides from ash from 70 to about 90 percent.

#### DEVELOPMENT & TECHNICAL SERVICES

##### Lithium Fluoride

Lithium cells at Sebree are running satisfactorily. One lithium cell was lost in February as a result of sidewall failure. The failure was not attributed to the use of lithium. The lithium experiment is continuing with the three remaining cells. No plans have been made to add cells to the test.

Lithium additions to five Columbia Falls cells are scheduled to begin at the end of March. Target parameters will be 2-2.5 weight percent LiF and 1.38

cryolite ratio. Plant personnel are currently collecting base data on the test cells.

A literature search on lithium fluoride was completed. Articles are on order. An outline for a position paper on lithium economics has been completed.

#### Sebree Large Area Anode

The large anode test is nearing completion with normal anodes being phased back in on three of the four test posts. Large anodes will be set in the modified sidewall test pot for two additional weeks. Preliminary results indicate from 0.1 to 0.2 reduction in kwh/pound with large anodes. Sebree will issue a final report in April.

#### New X-ray Method

Mike Schneller issued a final report on his new x-ray method for cryolite ratio study. One advantage of the new method is its measurement stability whenever bath samples are contaminated with excess carbon and alumina. No other advantages between the new method and the standard methods were found.

#### Pot Magnetics

Working with Columbia Falls personnel, a magnetics measurement probe has been selected and ordered, and a sheath for the probe has been designed and fabricated. Tests are scheduled to determine temperature conditions within the sheath for compatibility with the probe.

#### Tucson Computing Requirements

A memorandum outlining Tucson's computing requirements was prepared. Emphasis was given to computer modeling, statistical analysis and economic analysis.

#### FACILITIES

Construction of the Carbon & Reduction Research lab continues on schedule. Requests for quotation are out for 80 percent of the equipment. Major equipment with long lead times has been ordered. The remaining equipment to be ordered are stock items with relatively short lead times.



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